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Heterogeneous Exchange of Amalgams. I. Zn-Amalgam-$Zn^{2+}(SO_4^{2-})$ Solution Exchange*

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The exchange between zinc ions in solution and zinc in amalgam has been investigated by the technique of radioactive indicators. It was found that there is a dependence between the exchange rate and content of zinc in solution, for a constant content of zinc in amalgam, of the form:

$$\log R = a + b \log n_L$$

The coefficients a and b were determined by the least squares method for 3.5×10^{-4} and 7×10^{-4} g atom of zinc in amalgam. The value of coefficient b close to unity, which is obtained for low concentration of zinc ions with 7×10^{-4} g atoms zinc in amalgam, indicates that diffusion of zinc ions through the interface solution-amalgam is the slowest process. For the region of amalgam concentrations with n_S higher than 7×10^{-4} g atom of zinc it may be concluded that the exchange rate does not depend on the zinc concentration in the amalgam.

INTRODUCTION

Isotopic exchange between metal amalgams and solutions of their corresponding ions is used for the separation of radioactive and stable nuclides and for the study of the mechanism of electrode processes. Silker[1] has developed a technique of amalgam exchange for the separation of radioactive zinc from reactor cooling water with which radioactive zinc is obtained in high yields and free from other radionuclides. Meinke *et al.* have suggested procedures for the radiochemical separation of indium[2], strontium[3] and bismuth[4]. Riskin *et al.*[5] have found that the rate of isotopic exchange of potassium both in amalgam and solution is proportional to its concentration and that the influence of some foreign cations on the rate of exchange varies. The separation factor that Zuker and Drury[6] obtained in separating ^{46}Ca and ^{40}Ca by amalgam exchange was 1.0033. In investigating the kinetics of the exchange of cadmium salts at an equilibrium potential, Fronaeus[7] found that within the ranges of concentrations investigated (0.5 to 2.0% by weight) the rate of the total exchange was proportional to the concentration in the solution and independent of the solution and independent of the concentration in the amalgam phase. Pleskov and Miler[8,9] arrived at similar conclusions on investigating bismuth, lead and zinc amalgams. Haissinsky and Cottin[10] investigated the exchange of the Hg/Hg^{2+} system.

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The purpose of the present work was to investigate the phenomenon of exchange between metal amalgams and solutions containing appropriate ions in which are varied the factors influencing the state of the ions in the solution, the state of the interface and the state of metals. An explanation of these phenomena is important for both the separation of nuclides and the study of electrode processes, since by using the amalgam-solution system, the influence of the state of the surface and lag of diffusion in the metal can be eliminated. This work presents results of investigating the influence of the ion concentration in the solution and the content of metal in the amalgam on the rate of exchange in the Zn/Zn^{2+} system. The technique of radioactive indicators was used.

EXPERIMENTAL

The exchange was carried out in cylindrical glass cells (Fig. 1). There is an opening in the side of the cell through which the solution and amalgam are inserted and through which samples of the solutions are taken out for activity measurement. There is a thin tube along the cell wall through which inert gas is passed, it leaving through an opening at the top. Contact between the solution in the cell and the atmosphere was avoided by means of mercury or water stoppers. Seven cells were put in a water bath in which a temperature of 25 ± 1° C was maintained by circulation of water from an ultrathermostat. The exchange was performed in a nitrogen atmosphere. The solutions were made from a concentrated zinc sulphate solution prepared by dissolving zinc oxide in sulphuric acid. A constant ionic strength of 2M was obtained in all experiments by adding the required volumes of a 1 *M* solution of magnesium sulphate. The volume of the solution was 10.0 ml. and the *p*H was adjusted to 4.00 ± 0.05 with the aid of a *PHM* 4b *p*H-meter *(Radiometer,*

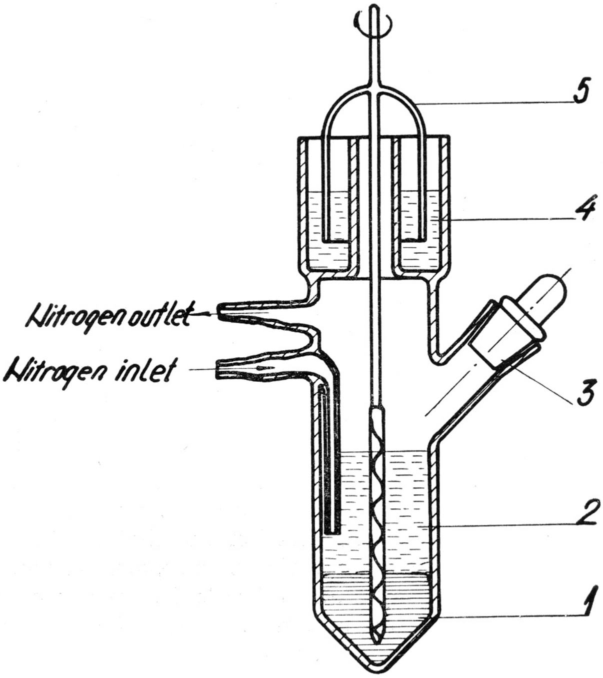

Fig. 1. Cells for exchange. (1) amalgam; (2) solution; (3) opening for sample taking; (4) stopper; (5) stirrer.

Copenhagen). Thus the concentrations in gatom per litre can be obtained by multiplying the n_L value with 100. Before adding the amalgam the solutions were thermostated in the cells for 30 minutes, together with the passage of nitrogen and stirring at 150 ± 20 r/min. The flow of nitrogen and the stiring were not interrupted throughout the experiment. Amalgam was prepared in an electrolyzer with a mercury cathode in a nitrogen atmosphere. Zinc was added in sulphate form in an electrolyte consisting of 1 *M* sulphuric acid and always the same amount of an active zinc sulphate solution containing radioactive zinc-65. Electrolysis was discontinued when there was less than 1% of the initial activity in the electrolyte. Two milliliter aliquots of amalgam were added to the cells with a special burette. Therefore the concentrations in gatom per litre can be obtained by multiplying the n_S value with 500. To avoid contact with the surface active substances, the sockets and taps were lubricated with water. All solutions were made of chemically pure substances and twice-distilled water.

The solution samples for activity measurement were taken with a 0.025 ml pipette washed once with distilled water. The samples were put in glass cells and the activity measured with *Nuclear Chicago DS 5* well-type scintillation counters. All measurements were made with a preset number of 1,000 counts which gives an error of 3%.

RESULTS

The results are expressed as percentages in the fraction of exchange against time or as the logarithm of unexchanged part against time. The fraction of exchange was calculated from the following formula:

$$F = (A_t - A_0)/(A_\infty - A_0) = A_t/A_0 \qquad (1)$$

A_t is the radioactivity of the solution at time t and A_∞ is the activity at equilibrium. The activity of the solution before exchange, A_0, is equal to zero, since the amalgam is labelled.

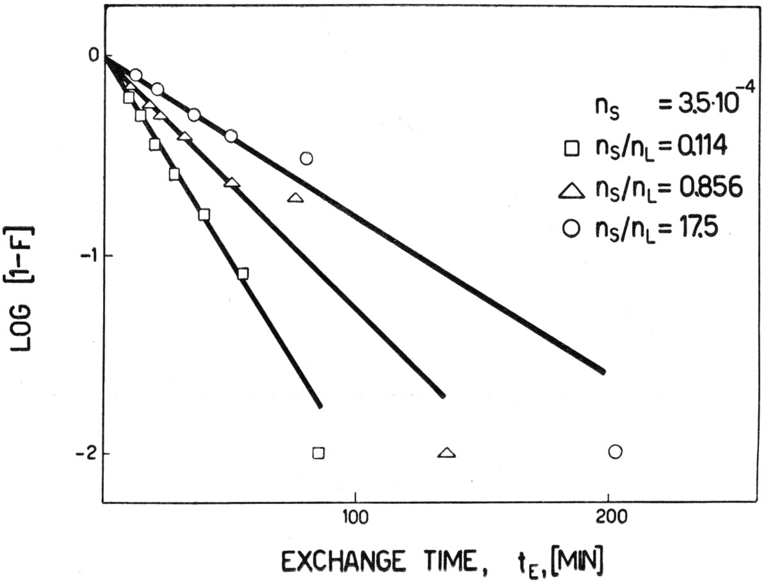

Fig. 2. Log (1—F) *vs.* exchange time.

Fig. 2 shows the results for several different n_L but equal $n_S = 3.5 \times 10^{-4}$ with log (1—F) plotted against time. Here n_L and n_S are g ions zinc in the

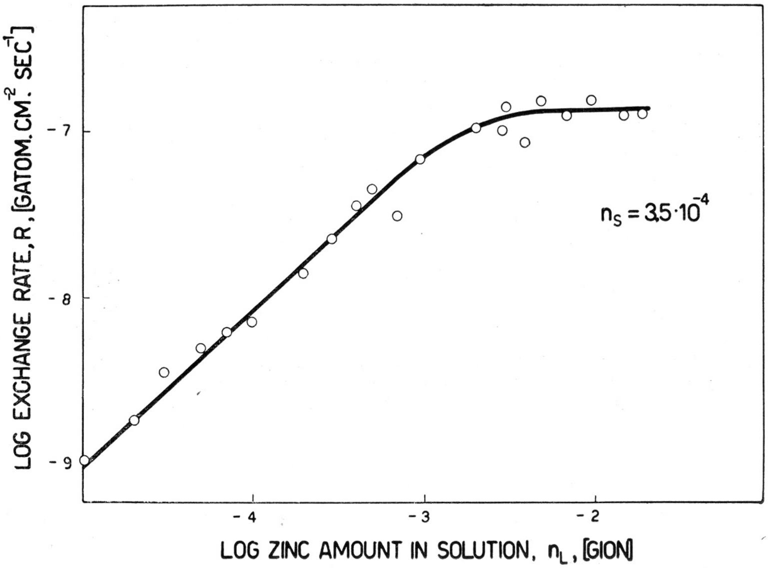

Fig. 3. Log exchange rate *vs.* log zinc amount in solution. Zinc amount in amalgam 3.5×10^{-4} g atom.

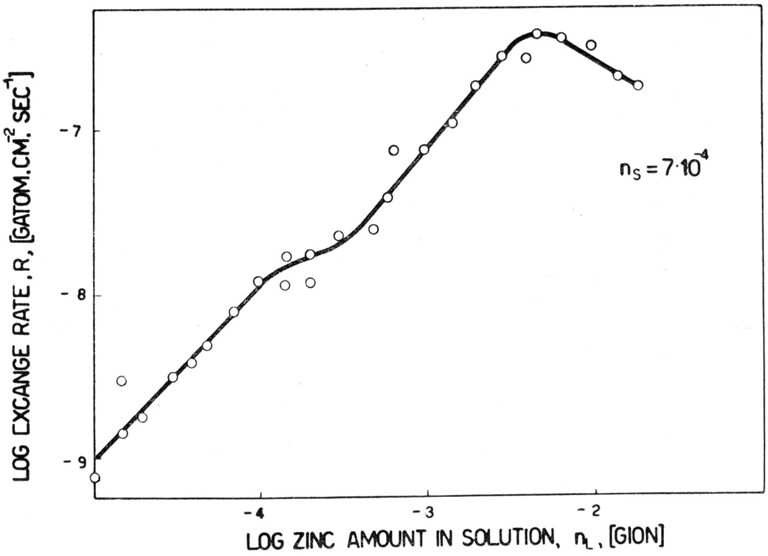

Fig. 4. Log exchange rate *vs.* log zinc amount in solution. Zinc amount in amalgam 7×10^{-4} g atom.

solution and g atoms of zinc in the amalgam. The linearity of log (1—F) against time in the region $0 < (1—F) < 1$ confirms that the exchange process takes place according to the first order reaction law and that the expression for the exponential exchange law of McKay can be used[11] to determine the velocity of exchange:

$$—Rts = [N_S n_L/(n_S + n_L)] \ln (1—F) \quad (2)$$

where R* is the exchange rate, g atom · cm^{-2} · sec^{-1}, t is the time, sec, s the contacting surface in cm^2, and F the fraction of exchange. Introducing into equation (2) the time of half-exchange $T_{1/2}$ and F = 0.5, we obtain an expression from which the exchange rate can be calculated

$$R = [n_s n_L/(n_s + n_L)]\,(0.693/T_{1/2} \cdot s) \tag{3}$$

It follows from Fig. 2 that the plots of log (1—F) against exchange time t_E may be considered linear.

In Fig. 3 the exchange rate is plotted against the amount of zinc in solution for $n_S = 3.5 \times 10^{-4}$ g atom of Zn. Fig. 4 shows the same dependence for $n_S = 7 \times 10^{-4}$ g atom of Zn. The equations that relate the velocity of exchange to the amount of zinc in solution are determined, by the least squares method, as linear functions of the form

$$\log R = a + b \log n_L \tag{4}$$

TABLE I

Influence of n_S on the coefficients *a* and *b*

n_S	Range of n_L	*a*	*b*
$3.5 \cdot 10^{-4}$	$1 \cdot 10^{-5}$ — $5 \cdot 10^{-3}$	—(4.76 ± 0.02)	0.84 ± 0.03
$7 \cdot 10^{-4}$	$1 \cdot 10^{-5}$ — $1 \cdot 10^{-4}$	—(3.79 ± 0.04)	1.04 ± 0.12
$7 \cdot 10^{-4}$	$3 \cdot 10^{-4}$ — $5 \cdot 10^{-3}$	—(2.95 ± 0.06)	1.41 ± 0.15

Table I gives the values for *a* and *b*. It may be seen that coefficient *b* is one for $n_S = 7 \times 10^{-4}$ at the lower concentrations of zinc in solution, while at the higher concentrations it is greater than one.

Fig. 5. shows the relation between log R and log n_S for constant n_L. The values are obtained from the curves calculated by the least squares method for $n_L = 2 \times 10^{-5}$ g ions of Zn. From this graph it may be concluded that for low n_S the dependence is linear, while for high velocities of exchange it is constant for all n_S.

DISCUSSION

According to Zimens[12], for heterogeneous exchange in systems with phases which differ in their transporting media (*e. g.* in their density and viscosity) as is the case here, the velocity of exchange, unless depending on diffusion through a layer of less dense phase and on the reaction at the interface, may even depend on the transport of mass in the denser phase. The slowest process is the rate-determining process of exchange. If the transport of mass in the denser phase is rate-determining, the situation becomes complicated, so that the exchange exponential law obtains another term — a constant which depends on the shape of the interface of the two phases. If this is the case there is no linear dependence between log (1—F) and time. It follows from Fig. 2 that under our conditions the kinetics of the zinc amalgam exchange is a typical example of the linear dependence between log (1—F) and time. If we take this linearity as a sure sign that diffusion in the amalgam does not infuence

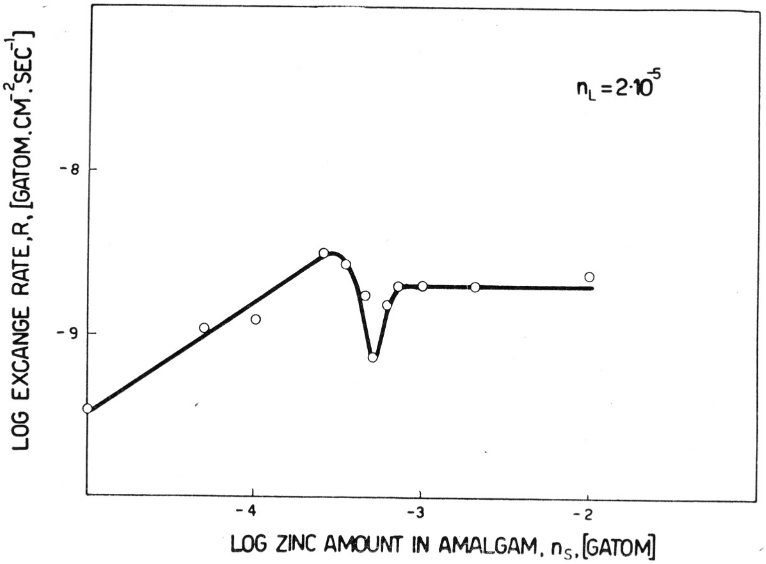

Fig. 5. Log exchange rate *vs.* log zinc amount in amalgam. Zinc amount in solution 2×10^{-5} g ion.

the kinetics of exchange, then there remain two other processes: diffusion of zinc ions through the boundary layer or exchange of Zn atoms in the zone of greatest approach (in which loss and bonding of ligands are included). If the diffusion of zinc ions is the slowest process, the velocity of exchange should be proportional to the concentration of zinc in the solution[13], *i. e.* the value of coefficients *b* in equation (4) should be equal to unity. It may be seen from Table I that coefficient *b* for amalgam, with $n_S = 3.5 \times 10^{-4}$ g atoms of zinc, is equal to 0.84 ± 0.03, while for amalgam with $n_S = 7 \times 10^{-4}$ it is equal to 1.04 ± 0.15, both these results are for the regions of lower concentrations of zinc ions. From these results it may be concluded that in the given regions of concentrations for $n_S = 7 \times 10^{-4}$ g atom of Zn, the diffusion of zinc ions through the boundary layer is rate-determining.

The dependence of the exchange rate on the amount of zinc in amalgam for a constant amount of zinc in solution is interesting (Fig. 5). It may be assumed that at low concentrations, zinc has the form in which the chemical activity is proportional to the concentration, while in higher concentrations this activity seems to be independent of concentration.

For comparison Table II shows the values of the exchange rate obtained in our experiments and those obtained by other authors. Although the experimental conditions differ, the exchange rates are of the same order of magnitude.

In his studies on cadmium exchange, Fronaeus[7] arrived at the same results: that the exchange rate is proportional to the amount of metal ions in solution. His conclusion that the amount of metal in the amalgam does not influence the velocity of exchange is in agreement with our results as can be seen from Fig. 5, for the range of the concentration of zinc in amalgam higher than $n_S = 7 \times 10^{-4}$ g atom. Fronaeus measured the exchange in the range of concentrations 0.5 — 2.0 per cent by weight corresponding to our $n_g = 2.0 — 8.6\ 10^{-8}$ g atom.

TABLE II

Values of the Exchange Rate for Zinc Amalgam

Composition of amalgam mol	Composition of the solution	Exchange current* a · cm^{-2}	Reference
0.13	0.025 *M* $ZnSO_4$ + + 0.975 *M* $MgSO_4$	5.24×10^{-3}	(14)
0.13	0.001 *M* $ZnSO_4$ + + 1.999 *M* $MgSO_4$	6.3×10^{-4}	(15)
0.17	0.025 *M* $ZnSO_4$ + + 1.975 *M* $MgSO_4$	3.5×10^{-3}	our work
0.17	0.001 *M* $ZnSO_4$ + + 1.999 *M* $MgSO_4$	2.5×10^{-4}	our work

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IZVOD

Heterogena zamjena amalgama. I. Zamjena Zn-amalgama i otopine $Zn^{2+}(SO_4^{2+})$

A. Filip i M. Mirnik

Ispitivana je zamjena između Zn^{2+} iona u otopini i Zn u amalgamu tehnikom radioaktivnih indikatora. Utvrđeno je da se može međusobna zavisnost između brzine zamjene i sadržaja Zn^{2+} u otopini uz konstatni sadržaj Zn u amalgamu izraziti jednadžbom

$$\log R = a + b \log n_L$$

R je brzina zamjene a n_L količina Zn^{2+} u otopini. Metodom najmanjih kvadrata određeni su koeficijenti *a* i *b* od 3.5×10^{-4} i 7×10^{-4} gatom/min Zn u amalgamu.

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* The exchange current is obtained by multiplying the values for the velocity of exchange by $nF = 1.93 \times 10^5$, where *n* is the number of electrons participating in the reaction; *F* is the Faraday.

Vrijednost koeficijenta *b* bliza jedinici za niske koncentracije Zn^{2+} uz 7×10^{-4} gatom Zn u amalgamu ukazuje da je difuzija kroz površinu amalgam-otopina najsporiji proces. U području koncentracija Zn u amalgamu višim od 7×10^{-4} gatom po ml može se zaključiti da je brzina zamjene neovisna o koncentraciji Zn u amalgamu.

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